Model Quality Assurance Manual

For a Small Wastewater Treatment Plant Laboratory

This model Quality Assurance (QA) manual is intended for use by small wastewater treatment plants as a guide for designing and documenting the quality assurance program in their labs. When using this model manual, the user must remember that the town of Cascade, a fictitious town for the purposes of this Procedural Manual, uses one way of getting the job done. There are many others. Those who might have seen or used the "Cascade Model QA Manual" will recognize that this is an abbreviated version of that manual. Some features of the "Cascade" QA program (e.g., control charting the results of duplicate sample analyses) were not considered necessary for demonstrating that a small WTP lab is "in control." Those features may be necessary for larger labs.

The only hard and fast rule in doing analyses in the lab is that standardized methods (e.g., EPA methods, Standard Methods methods, ASTM methods) be followed as required by Federal (EPA) regulations. Wherever Cascade did something one way, the user of the model should ask "Is this the way I want to do it and, if not, is the way I do it allowed for wastewater monitoring?" If the answer is "yes" and there is no desire or need to change, the manual should be written up the way the lab is currently doing the job.

In places where the user might want to consider other ways of doing things, there are notes (a bold slash followed by a number---e.g., **/4)** to draw the user's attention to further guidance at the end of the manual. The notes are not intended to be part of the lab's finished manual.

When using this model QA manual to help in preparing for accreditation of a lab, keep in mind that to be accredited, lab personnel must first convince themselves that the lab is in control (meeting quality objectives). If they can do that, they should be able to convince Ecology the lab is in control. The **easiest** way to do both (convince themselves **and** Ecology) is to keep control charts, especially for standards such as the BOD and TSS standards mentioned in the model. The control charts take a little effort to set up, but after that, they are easy. Assistance is available from Ecology's QA Section in setting up and using control charts.

If a user of this model has any questions on either the manual or on quality assurance in general, the lab's team leader in the Lab Accreditation Unit should be contacted at (360) 895-4649. If a team leader has not been appointed or the lab is not sure of who it might be, call the number and ask to speak to anyone about the issue of concern.

City of Cascade Wastewater Treatment Plant
QUALITY ASSURANCE MANUAL

August 9, 2000

1. Organization/Responsibilities

The Cascade Wastewater Treatment Plant (FWWTP) is operated by a senior operator and two assistant operators. The senior operator is responsible for establishing quality assurance and quality control (QA/QC) policies and ensuring those policies are followed. The senior operator is also the primary laboratory analyst and is responsible for performing analyses on wastewater and quality control samples and recording results. In the absence of, or under the direct supervision of the senior operator, the assistant operators may also perform analyses on wastewater and QC samples and record results. The senior operator will verify such results. The senior operator is also the sample custodian.

2. Policy for Quality Assurance/Quality Control

a. The principal objective for operating the FWWTP laboratory is to consistently produce complete analytical data which accurately represent the waste stream from which that samples are taken.

b. All analytical procedures will be completed according to approved methods (specified in paragraph 4 of this manual) and will include all QA/QC measures required by those methods. The initial data quality objective (DQO, a target for precision, and for accuracy, which involves bias as well as precision) for each method is to achieve better precision and accuracy levels than those cited for each method in "Standard Methods". Once control charts have been established for BOD and TSS (see paragraph 5h(3) below), the statistics used for the chart (i.e., the mean and standard deviation) become the DQOs for those tests, provided they are better than the initial DQOs.

c. No sample data will be recorded without including results for any analyses of QC samples associated with the data. Data will be entered in indelible ink on printed bench sheets and kept in binders. Data will be kept for at least three years. All data is reviewed and validated prior to release of the data from the FWWTP laboratory.

d. Initial training for new operators on analytical methods and QA/QC requirements and procedures will be conducted on a priority basis. Additional training is be conducted periodically (not less frequently than twice per year) as required to maintain competence in analytical skills. Records of all training are kept in each trainee's personnel folder.

g. Located in the lab are copies of the FWWTP discharge permit, "Standard Methods," applicable EPA methods, this QA Manual, and, in a readily available binder, safety data sheets for all potentially hazardous chemicals used in the lab.

3. Sample Management

a. Samples are be taken according to the schedule in Table 1 (at the end of this section /**1** f the manual) which includes preservation techniques and maximum holding times. Daily samples, including collection of composited samples, are taken between 9:00 and 10:00 a.m., and weekly samples on Wednesday mornings (same time) unless conditions (e.g., weather, plant

operations, personnel availability) do not permit sampling at that time. In such cases, samples are taken as soon as possible and a note made in the plant log justifying the delay. /**2**

b. The senior operator as sample custodian assures: (1) samples are stored properly and handled by a minimum number of people; (2) the lab is secured at all times when not in use; (3) only authorized personnel are allowed in the lab; (4) samples are logged on permanent lab record, and; (5) someone is designated to analyze the sample.

4. **Methods**

Methods used in the FWWTP lab are those prescribed in the 17th Edition of "Standard Methods for the Examination of Water and Wastewater" Method numbers are indicated in Table 1. Appendix D is a brief description of the methods used in the FWWTP lab. **/3**

5. **Calibration and Quality Control Procedures**

a. Lab Facility. The lab is kept clean and orderly at all times. Specific facility issues are addressed in the checklist at Appendix C.

b. Instrument Calibration. Instruments are calibrated on a daily basis just before use and every two hours during prolonged periods of use on any given day. Those requiring calibration are the pH meter and probe, and the DO meter. The DO meter is normally calibrated against saturated air but, once each week, is calibrated using a Winkler titration. Records of calibration are maintained on log sheets for each piece of equipment. Equipment calibration requirements **/4** are indicated in Table 2 (at the end of this section of the manual).

c. Preparation of Calibration Curves. No calibration curves are required in this lab. **/5**

d. Equipment Maintenance. All lab equipment is maintained so as to keep it in proper working order at all times. Simple repairs may be made by lab personnel; qualified service representatives will perform more extensive repairs. Breakdowns and repair procedures are noted in the log on each piece of equipment. Checks of the drying oven, water bath and/or incubator temperatures are performed and recorded. The analytical balance is checked monthly or more often using standard weights and serviced by professional service representatives as required or, as a minimum, annually. The dissolved oxygen membrane is replaced every two weeks or more often if readings become erratic. A backup probe is kept on hand in case of probe failure. Records of all routine maintenance and repairs are kept in equipment logs. The sample refrigerator is maintained at a temperature between 1 and 4.4°C.

e. Analytical Reagents. Only analytical grade reagents are used. Labels on all chemical reagents are marked with date received, date opened, and, when known, date of expiration. Chemicals are stored out of direct sunlight. Those requiring cold storage are kept in the refrigerator, separate from sample storage. Acids and bases are stored separately in specially designated areas. Care is taken to prevent cross contamination of reagents and samples. Contaminated reagents and outdated chemical solutions are disposed of in accordance with accepted practices. For reagents mixed in the lab, shelf life recommendations provided in the analytical method are followed and bottles are marked with date prepared and the initials of the analyst. Distilled water, produced in the lab using a still, is stored in glass carboys (water may be purchased when necessary). Care is taken not to contaminate distilled water, and water suspected of being contaminated is discarded. Standard solutions are stored separately and safeguarded to **/6** preclude inadvertent contamination.

f. Labware Cleaning. After each use, glassware is washed with phosphate-free (environmentally friendly) detergent, rinsed with tap water, rinsed with distilled water, **/7**

allowed to dry, and stored in a cabinet. When siphon tubes are used for BOD dilution water, they are cleaned weekly with a bleach solution (25 mL of household bleach per liter of water) and rinsed thoroughly (additionally, they are flushed just prior to use with dilution water). Sample bottles and equipment for microbiological evaluations are sterilized in accordance with Standard Method 904 (Edition 16).

g. Quality Control Analyses. Quality control measurements are made for all analyses related to "plant performance" samples (as indicated by "PP" in Table 1). It is very important that these tests be performed exactly as written in published methods. Routine analyses of blanks, duplicates, and standard solutions are performed according to the frequency shown in Table 2. Results of blank analyses are treated in the manner specified by the method. Data from results of duplicate analyses are compared to data quality objectives stated in the following subparagraphs. Records of analyses of standard solutions (i.e., the glucose/glutamic acid test for BOD, and the cellulose standard for TSS) are kept on daily bench sheets (See Appendix B for format). The are also recorded on the plant sample bench sheets. QC considerations for specific tests follow.

(1) BOD. The DO probe is air calibrated each day during which analyses are **/8** normally run or once every two hours during prolonged runs. Samples are incubated at 20±1°C as measured by a certified thermometer (i.e., one which has been checked against a National **/9** Institute of Standards and Technology---NIST---thermometer). It is very important that initial DO be measured when the sample is at 20±1°C so initial and final DO are measured at the same temperature. Dilution water is kept in the incubator to make sure it is at 20±1°C. If necessary, samples are warmed or cooled to bring them to the same temperature. A freshly prepared check standard consisting of 150 milligrams each of glucose and glutamic acid dissolved in one liter **/10** of distilled water is analyzed (using a settled primary effluent seed) at a rate of one weekly. If the BOD of the check standard is outside the action range on the control chart, the source of the problem is sought, and corrected. Duplicates are run monthly on final effluent samples. Duplicate results should give a relative percent difference (RPD---see Appendix A of this QA Manual for a definition) of 20% or less. A blank is run on unseeded dilution water with each set of samples.

Depletion (i.e., the DO drop) on the blank should not exceed 0.2 mg/l, and DO drop for samples should be at least 2 mg/L with a residual DO of at least 1 mg/L. If these targets are not met, corrective action is taken (e.g., calibration, dilution water, and the nutrient solution are checked, and problems corrected). A performance evaluation (PE) sample is analyzed once every six months as part of a EPA's Water Pollution (WP) Study. If results are not within acceptable limits, a QC sample is analyzed after identifying and correcting probable causes of error.

(2) Total Suspended Solids (TSS). The principal calibration in the TSS determination is on the analytical balance which is checked by lab personnel monthly using class "S" weights (borrowed from a nearby lab), and by a service representative annually. A check standard prepared in the lab using micropulverized (20 micron) cellulose, is analyzed once per **/11** week. A blank is run on deionized water each test. If TSS value for the blank is more than 20% of the average value for the last ten TSS sample analyses, the cause is sought and, if necessary, **/12** corrective action is initiated. Duplicates are run monthly on effluent samples. The duplicate values should give an RPD of 30% or less. EPA PE samples are analyzed as in 5g(1) above.

(3) pH. The manufacturer's instructions are followed for storage and preparation for use of the pH meter. Two buffer solutions are used to calibrate the meter, one at approximately 2 pH units from the expected sample pH, and the other bracketing the pH expected for most samples and within 3 pH units of the first (e.g., at pH 4 and 7 for slightly acidic samples, and pH 7 and 10 for slightly basic samples). Calibration is checked just prior to use and once every two hours during prolonged runs, with two of the buffer solutions. A check standard, prepared as a buffer solution but separately from the buffer solutions prepared for meter

calibration, is analyzed monthly. Duplicates are run monthly on effluent samples. Duplicate values should not vary by more than 0.1 pH unit. Performance evaluation samples are analyzed as in 5g(1) above.

(4) Chlorine Residual. There are no instruments requiring a calibration curve especially for chlorine residual determinations (the instrument is zeroed, but not calibrated with known standards). A check standard, obtained from a commercial source, is analyzed once per quarter. A blank is run on deionized water each day. Duplicates are run every month and should give an RPD of 20% or less. Performance evaluation samples are analyzed as in 5g(1) above.

(5) Fecal Coliforms. There are no instruments requiring calibration for fecal coliforms determinations nor are there requirements for analyzing check standards. A blank is run with each set of samples. The filter in the blank determination is rinsed with buffer solution to make sure the buffer is not contaminated. Duplicates are run every month and should give an RPD of 30% or less. The normal method for determination of fecal coliforms in the FWWTP lab is the membrane filter (MF) technique. As a quality control check on the MF method, the lab splits a sample twice annually with a lab having a most probable number (MPN) capability. If the MF value is not 80% or more of the MPN value, causes are sought and remedied, where possible, and the comparative process repeated. Quarterly, the lab exchanges samples with a nearby wastewater plant lab as an interlab check on the accuracy of fecal coliform tests.

h. Evaluating Accuracy. The ability of the lab to perform accurate analyses is evaluated by analyzing quality control samples.

(1) Check standards (samples of concentration known to the analyst) are used primarily to check on bias and precision. Check standards are analyzed infrequently for pH and residual chlorine and more often for TSS and BOD (see Table 2 for frequency). There is no check standard for fecal coliforms. By preparing a control chart using the results of several analyses of the same standard, the lab monitors overall accuracy by comparing the mean or average value **/13** of all results to the true or expected value. The lab also monitors precision by plotting individual results on the control chart.

(2) PE samples (samples of concentration unknown to anyone in the FWWTP lab, but known to the supplier of the sample) are used as a check on overall accuracy. PE samples for all plant performance parameters listed in Table 1 except fecal coliforms are analyzed twice per year as part of the EPA's WP studies using samples currently provided free of charge by EPA.

(3) To evaluate precision of analysis for BOD and TSS, control charts are maintained for appropriate determinations. If problems are encountered in pH tests, control charts may also be used for pH. The control charts are based on analysis of the standard solution for BOD and the standard suspension for TSS. After a minimum of ten (but preferably 20) replicates of the standard solution for a given parameter have been completed, the standard deviation for the analysis is calculated using the worksheet at Appendix B. Appendix B also includes an example of a completed worksheet. Using the calculated standard deviation (s), a control chart is constructed as shown in Appendix B. Concentration of the standard solution is indicated on the chart in Appendix B as X.0 mg/l. Where the chart below indicates +3s, for example, the actual control chart would indicate a value of the standard solution concentration (or mean of 10-20 replicate results) plus three times the calculated standard deviation. Likewise, -3s indicates the standard solution concentration minus three standard deviations. Page 13 shows a control chart based on the data presented on Page 12.

Once the control chart has been constructed, all subsequent determinations of the same standard are plotted on the control chart. As long as the values are within the action limits, values for samples analyzed in conjunction with the standard may be reported. If a value exceeds either

action limit, if more than three consecutive values exceed one warning limit, or if more than seven consecutive values are on one side or the other of the central line, the lab is out of control for that analysis. Analysis for that parameter must cease until the situation is investigated, the cause found, and corrective actions taken. When a chart becomes cluttered or whenever there is a significant change in procedure (e.g., a new analyst takes over the test) new control charts are constructed based on standard analyses for the past 20 results. The points on the sample control chart on Page 13 represent analyses of the standard solution taken after constructing the basic chart.

6. **Data Management**

All records mentioned in the preceding and subsequent paragraphs and required in standard methods are retained at the FWWTP office in file cabinets for a period of at least three years. Before any result is reported, all raw data and calculations are reviewed for accuracy and signed by the senior operator acting as the quality assurance officer. If data contained on any record is transcribed to facilitate brevity or neatness, the original record is also kept. All data is recorded in ink and corrections are initialed. A list of initials identifying the person to whom they belong is maintained as a permanent lab record.

7. **Audits**

Two types of audits are used to determine status of the FWWTP lab operations. A system audit is used to assess personnel, equipment, facilities, and analytical procedures. The system audit is conducted periodically by the Department of Ecology and at least every six months by the senior operator. Performance audits are conducted at least once every six months for each plant performance parameter except fecal coliforms as part of the EPA Water Pollution Study.

8. **Reports**

A QA/QC report is prepared quarterly and given to the senior operator. The senior operator may provide the report in writing (verbatim or in summary) or verbally to the City Engineer. The checklist at Appendix C is used to assist in drafting these reports and otherwise in assessing lab capability and performance.

APPENDICES:

A - Glossary of Common QA Terms
B - Control Charting Standards
C - Laboratory Quality Assurance Checklist
D - Summary of Analytical Methods

APPROVED:

_____
Patty O'Rourke
Senior Operator, FWWTP

TABLE 1

UNIT PROCESS	SAMPLING LOCATION	ANALYSIS	SAMPLE USE	SAMPLE FREQ	SAMPLE TYPE	STANDARD METHODS*	PRESERVATION	HOLDING TIMES	CONTAINER REQUIREMENTS
Primary Treatment	Primary influent	BOD	PP	D	C	5210B	Cool, 4°C	6 hours	P, G
		TSS	PP	D	C	2540D	Cool, 4°C	7 days	P, G
		pH	PC	W	G	4500-H	None Required	Stat	P, G
	Primary effluent	BOD	PP	W	C	5210B	Cool, 4°C	6 hours	P, G
		TSS	PP	W	C	2540D	Cool, 4°C	7 days	P, G
		F Col	PP	D	G	9222D	Cool, 4°C 0.008% $Na_2S_2O_3$	6 hours	P, G
		pH	PP	D	G	4500-H	None Required	Stat	P, G
Activated Sludge	Primary effluent	BOD	PP	D	C	5210B	Cool, 4°C	6 hours	P, G
		TSS	PP	D	C	2540D	Cool, 4°C	7 days	P, G
		pH	PC	D	G	4500-H	None Required	Stat	P, G
	Mixed liquor	DO	PC	D	G	4500-O	None Required	8 hours	P, G
		Temp	PC	D	G	2550	None Required	Stat	P, G
		TSS	PC	D	C	2540D	Cool, 4°C	7 days	P, G
		NO_3	PC	D	G	EPA 352.1		48 hours	P, G
	Return sludge	TSS	PP	W	C	2540D	Cool, 4°C	7 days	P, G
	Final effluent	BOD	PP	D	C	5210B	Cool, 4°C	6 hours	P, G
		TSS	PP	D	C	2540D	Cool, 4°C	7 days	P, G
		F Col	PP	D	G	9222D	Cool, 4°C, 0.008% $Na_2S_2O_3$	6 hours	P, G
		Cl Res	PP	D	G	4500-Cl	None Required	Stat	P, G
		pH	PP	D	G	4500-H	None Required	Stat	P, G

* 17th Edition unless otherwise indicated.

Cl Res	=	Chlorine residual	TSS	=	Total Suspended Solids	D	=	Once per day	F Col	=	Fecal coliforms
VS	=	Volatile solids	W	=	Once per week	NO3	=	Nitrate nitrogen	PP	=	Plant performance
G	=	Grab	Temp	=	Temperature	PC	=	Process control	C	=	Composite
TS	=	Total solids	VSS	=	Volatile suspended solids	P,G	=	Plastic or glass			

TABLE 2

QUALITY CONTROL PROCEDURES FREQUENCY CHART

Parameter	Calibration	Check Standards	Blanks	Duplicates	PE Samples
DO (for BOD procedure)	N/A for Winkler titration. If using DO probe, air calibrate each day	1 per week	Each day [1]	1 per month on final effluent	1 every 6 months
TSS	Balance check each month & each year by a service rep	1 per week	Each day [1]	1 per month on final effluent	1 every 6 months
pH	Each day	1 per month	N/A	1 per month on final effluent	1 every 6 months
Chlorine residual	N/A	1 per quarter	Each day [1]	1 per month	1 every 6 months
Fecal Coliforms	N/A	N/A	With every set of samples	1 per month	N/A

NOTES: 1. "Each day" above means each day that analyses are normally run.

APPENDIX A

GLOSSARY OF QUALITY ASSURANCE/QUALITY CONTROL TERMS

Accuracy	Degree of agreement of an analytical result with the true value. Accuracy is affected by both random and systematic errors, but is sometimes used (improperly) to denote only systematic error. (See **Bias** below.)
Action Limit	A type of control limit on a control chart, which, if exceeded, requires corrective action to be taken. Action limits are usually place at ±3 standard deviations from the expected or mean value.
Batch	A set of consecutive determinations (analyses) made without interruption: a "run". Results are usually calculated from the same calibration curve or factor.
Bias	That part of inaccuracy of analytical results caused by systematic error.
Blank	An analysis made by the same procedure as a sample, but intended not to contain the determinand (analyte). (In water analyses, pure water would be analyzed to determine the blank.)
Check Standard	A solution of known concentration that is used to check the precision of analyses (and bias due to calibration). When used in conjunction with a control chart it becomes a control standard. Check standards are prepared from different sources than standards used for calibration.
Data Quality Objectives (DQOs)	Qualitative and quantitative statements of the quality of data needed to support specific decisions or regulatory actions. Quantitative statements address accuracy, completeness, representativeness, and defensibility as a minimum, and quantitative statements should address bias and precision.

Precision

A qualitative term used to denote the scatter of results. Precision is said to improve as the scatter among results becomes smaller. Also referred to as imprecision. Precision is usually measured as standard deviation or relative percent difference (RPD).

Quality Assurance (QA)

The total integrated program for ensuring the reliability of monitoring and measurement data.

Quality Control (QC)

The routine application of statistically based procedures to evaluate and control the accuracy of results from analytical measurements.

Random Errors

Errors occurring when repeated analyses of identical portions of a homogeneous sample do not give a series of identical results. The results differ among themselves and are more or less scattered about some value. They are termed random because the sign and magnitude of the error of any particular result vary at random, and cannot be predicted exactly.

Relative Percent Difference (RPD)

The difference between duplicate results for analyses of a sample, relative to the mean (average) value of those results, and expressed as a percent.

$$\text{RPD} = \frac{100(R_1 - R_2)}{(R_1 + R_2)/2}$$

$$= \frac{200(R_1 - R_2)}{(R_1 + R_2)}$$

where "R_1" is the result of the first analysis, and "R_2" the second.

Relative Standard Deviation (RSD)

The standard deviation relative to the mean (also called coefficient of variation). It is calculated as either:

$$s / \bar{x} \quad \text{or} \quad 100s / \bar{x}$$

RSD,Cont'd

Where $\bar{x}$ is the mean result and s is the standard deviation (see **Standard Deviation** below). $100s / \bar{x}$ is sometimes referred to as the percent relative standard deviation or %RSD.

Standard

A solution of known concentration, either a "check" or "control" standard, or a calibration standard that is used to prepare a calibration curve.

Standard Operating Procedure (SOP)

A detailed written description of a procedure designed to systematize performance of the procedure.

Standard Deviation

A constant that describes the spread of results. An actual standard deviation is denoted by "σ", whereas an estimate of the standard deviation is denoted by "s". For a sample of "n" replicate results taken from a population of sample analyses of known concentration, the estimate of the standard deviation is:

$$s = \sqrt{\frac{x_i^2 - \left| \left(x_i \right)^2 / n \right|}{n-1}}$$

$$= \sqrt{\frac{x_i^2 - n\left(\bar{x}\right)^2}{n-1}}$$

$$= \sqrt{\frac{\left(x_i - \bar{x}\right)^2}{n-1}}$$

where x_i is a result and $\bar{x}$ is the mean of "n" results. For duplicate analyses of "m" pairs of unknown samples, the estimate of standard deviation of the difference (d) for the two samples in each pair is:

$$s = \sqrt{\left(d_i^2 \right) / 2m}$$

Systematic Errors	Errors that are indicated by a tendency of results to consistently be greater or smaller than the true value. Usually, bias can be consider to be equivalent to systematic error.
Warning Limit	A type of control limit that is specified by a value on a control chart, usually ±2 standard deviations distant from the expected or mean value. Action is required when results fall outside the warning limits too frequently. A single value outside a warning limit does not require action, but should alert one to a possible problem. Three consecutive results outside a warning limit should be cause for action.

APPENDIX B

BENCH SHEET FOR REPLICATES OF STANDARD SOLUTIONS

Parameter: _____ Method: _____

TEST (n)	DATE	RESULT (X)	$(X - \overline{X})$	$(X - \overline{X})^2$
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
		$X =$	$(X - \overline{X})^2 =$ A	
		$\overline{X} =$ $X/n =$		

Standard Deviaion = $s = \sqrt{A/(n-1)} =$

APPENDIX B

EXAMPLE OF COMPLETED BENCH SHEET -- STD SOLUTIONS

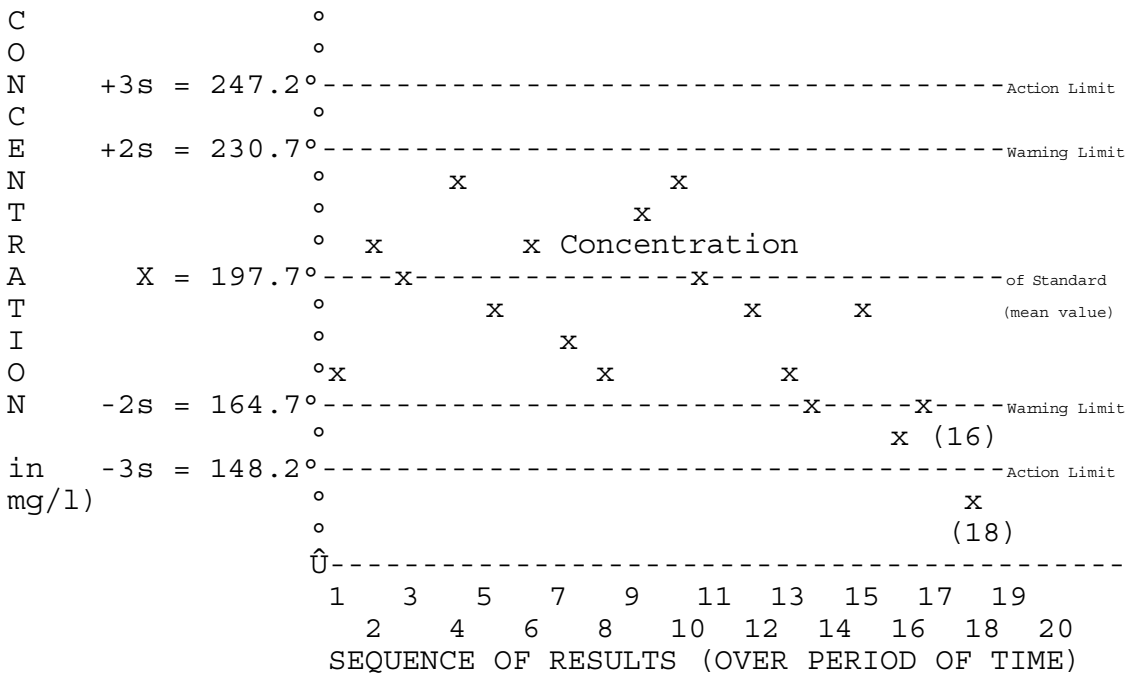
Parameter: BOD Standard Solution Method: SM 5210 B

TEST (n)	DATE	RESULT (X)	$(X - \overline{X})$	$(X - \overline{X})^2$
1	07/02/96	212	14.3	204.49
2	07/03/96	208	10.3	106.09
3	07/05/96	186	-11.7	136.89
4	07/06/96	202	4.3	18.49
5	07/08/96	190	7.7	59.29
6	07/09/96	178	-19.7	388.09
7	07/11/96	226	28.3	800.89
8	07/12/96	214	16.3	265.69
9	07/14/96	182	-15.7	246.49
10	07/15/96	179	-18.7	349.69
11	08/02/96	212	14.3	204.49
12	08/03/96	208	10.3	106.09
13	08/05/96	186	-11.7	136.89
14	08/06/96	202	4.3	18.49
15	08/08/96	190	-7.7	59.29
16	08/09/96	178	-19.7	388.09
17	08/11/96	226	28.3	800.89
18	08/12/96	214	16.3	265.69
19	08/14/96	182	-15.7	246.49
20	08/15/96	179	-18.7	349.69
$X = 3954$			$(X - \overline{X})^2 = 5152.2 = \text{A}$	
$\overline{X} = X/n = 197.7$				

$$s = \sqrt{A/(n-1)} = \sqrt{5152.2/(20-1)} = \sqrt{271.2} = 16.5$$

BOD STANDARD SOLUTION CONTROL CHART

Mean Conc'n of Std Sol'n 197.7 mg/l Std Deviation 16.5 mg/l



Results of Replicate Analyses obtained after the chart was made:

1	170	6	211	11	196	16	155
2	210	7	180	12	186	17	164
3	197	8	170	13	170	18	138
4	220	9	218	14	164	19	
5	185	10	225	15	188	20	

NOTE: After calculating a standard deviation (as on Page 12), the control chart shown above (without the "x" data points) was constructed. Subsequent analyses of the standard solution, as indicated in the "Results of Replicate Analyses" were then plotted on the chart with an "x". The above chart shows the procedure was in control on analyses #1-15 but exceeded the warning limits on #16. At that point, the analyst might have investigated possible causes and taken corrective actions, but is not required to do so. By #18, the procedure was out of control (beyond the action limit on the low side). The analyst should cease doing BOD's at that point until the problem has been corrected.

APPENDIX C

FWWTP LABORATORY QUALITY ASSURANCE CHECKLIST

	Yes	No	Comments
General			
1. Is Quality Assurance Manual up-to-date, available to all lab personnel?	____	____	_____
Laboratory Procedures			
1. Are EPA-approved methods (e.g. Standard Methods) used and readily available to and used by all lab personnel?	____	____	_____
2. Are calibration and maintenance of instruments/equipment satisfactory?	____	____	_____
3. Does a written schedule for required equipment maintenance exist?	____	____	_____
4. Are QC procedures in the QA Manual used consistently?	____	____	_____
5. Are QC records adequate to determine if lab is in control?	____	____	_____
Laboratory Facilities and Equipment			
1. Is distilled or deionized water available (as required by the method)?	____	____	_____
2. Is dry, uncontaminated, compressed air available (if needed)?	____	____	_____
3. Is the fume hood air-flow measured periodically and is it adequate?	____	____	_____
4. Is the laboratory sufficiently lighted?	____	____	_____
5. Are adequate electrical sources available in the lab?	____	____	_____
6. Are instruments appropriate for the method and in good			

condition? ____ ____
_____

7. Are trouble shooting procedures and written requirements for daily operation of instruments available to each instrument operator? ____ ____
_____

8. Are standards available to perform required QC checks? ____ ____
_____

9. Is proper volumetric glassware used? ____ ____
_____

10. Is glassware cleaned? ____ ____
_____

11. Are solvents and standard reagents properly stored? ____ ____
_____

12. Are calibration and check standards frequently cross-checked? ____
____ _____

13. Are standards discarded after recommended shelf-life has expired? ____ ____
_____

14. Are reagent bottles marked with date received, opened, and, when known, with expiration date? ____ ____
_____

15. Are blanks run each day for appropriate analyses (e.g., BOD, TSS)? ____ ____
_____

16. Are sufficient SOPs on hand for lab operations (e.g., cleanup, hazard response)? ____ ____
_____

17. Are gas cylinders (if used) replaced at 100-200 psi? ____ ____

_____

18. Are the thermometers used in incubators (e.g., BOD and fecal coliform incubators) traceable to a NIST-certified thermometer? ____ ____

_____

Laboratory's Precision, Accuracy, and Control Procedures

1. Are duplicates analyzed for all analyses and are the results recorded? ____ ____

_____

2. Are control samples required by the QA Manual introduced into the train of actual samples to ensure valid data are being generated? ____ ____

_____

3. Are control charts maintained and used routinely? ____ ____

_____

4. Is the lab within control (i.e., is precision good)? ____ ____

_____

Data Handling and Reporting

1. Are round-off rules documented and uniformly applied? ____ ____

_____

2. Are significant figures established for each analytical procedure? ____ ____

_____

3. Are results checked by at least on person other than the analyst? ____ ____

_____

4. Are correct formulas used to calculate final results? ____ ____

_____

5. Do report forms exist to provide complete data documentation and permanent records and to facilitate data processing? ____ ____

_____

6. Are data reported in proper form and units? ____ ____

_____

7. Are lab records maintained for three years? ____ ____

_____

8. Is all data recorded in indelible ink with corrections initialed? ____ ____
   _____

9. Is a list of initials identifying to whom they belong filed in the lab? ____ ____
   _____

10. Are lab notebooks and pre-printed data forms bound permanently to provide good and defensible documentation? ____ ____
   _____

11. Does and efficient filing system exist? ____ ____
   _____

Laboratory Personnel

1. Are enough analysts present to perform necessary analyses? ____
   ____ _____

2. Do analysts have on-hand necessary references for procedures being used? ____ ____
   _____

3. Are analysts trained in procedures performed? ____ ____
   _____

APPENDIX D

SUMMARY OF ANALYTICAL METHODS

1. pH (SM #4500-H B)

pH is a numerical expression of the intensity of value of the acidity or basicity of the tested solution. At 25°C, A value of 7.0 indicates the solution is neutral. Values less than 7.0 are acidic; greater than 7.0 are basic. Sudden changes in pH values may be the result of illegal discharges of acid or base into the wastewater system. Extreme shifts in pH may cause damage to the treatment facility and/or the biological treatment process. **/14**

This lab uses the electrometric method for pH measurements. The manufacturer's instructions are followed closely on use of the pH meter and on storage and preparation for use of the electrodes. Electrodes are kept wet by returning them to the storage solution recommended by the electrode manufacturer whenever the pH meter is not being used. To prepare the electrodes for use, remove them from the storage solution, rinse with distilled water, and gently blot them dry with soft tissue. Bring both the sample and buffer solutions to room temperature, record the temperature, and adjust the temperature dial on the pH meter to this temperature.

Calibrate the pH meter by immersing the electrodes in a buffer solution which is within 2 pH units of the expected sample pH, and setting the meter to read the pH of the buffer solution. Remove the electrodes, rinse and blot dry, and immerse in a second buffer which is approximately 3 pH units from the first buffer and which brackets the expected sample pH. If the meter reads more than 0.1 pH units from the value expected for the second buffer, look for trouble with the electrodes or potentiometer. Repeat this calibration procedure for every batch of pH analyses. Because samples normally analyzed in the FWWTP lab are slightly basic, buffers normally maintained are phosphate (1:1 mixture of 0.025M potassium dihydrogen phosphate and 0.025M disodium hydrogen phosphate) which ranges from pH 6.85 to pH 6.95, and borax (0.01M) ranging from 9.14 to 9.39 at normal lab temperatures.

When reading pH of the sample, establish equilibrium between the electrodes and the sample by stirring the sample to ensure homogeneity. Values are reported to the nearest 0.1 pH units. Typical intra-laboratory tests result in standard deviations of $\pm$0.1 to $\pm$0.2 pH units over the pH range.

2. Chlorine Residual (SM #4500-Cl B)

Chlorine is added to water to destroy or deactivate disease- producing microorganisms. Residual chlorine may be present in waters reaching the wastewater treatment plant. Since chlorine is not stable in water solutions, its concentration in samples decreases rapidly. Exposure to sunlight or other strong light, or agitation reduces the quantity of chlorine in solutions. Samples to be analyzed for chlorine residual must be analyzed immediately after sampling.

Chlorine (hypochlorite ion, hypochlorous acid) and chloramines liberate iodine from potassium iodide at approximately pH 4 which is the basis for the residual chlorine test. The liberated iodine is titrated with phenylarsine oxide (PAO) using a starch indicator. **/15**

Standard and buffer solutions are prepared and stored according to documented procedures. The procedure calls for adding sample and starch indicator to an acetate-buffered solution of phenylarsine oxide and potassium iodide. Excess PAO is titrated with a standardized iodide

solution to the first appearance of blue color that persists after thorough mixing. Standardization of the PAO solution, a critical step, is conducted with care.

In a single analyst, single lab test of domestic sewage, for a mean residual chlorine concentration of 1.11 mg/L, the standard deviation was determined to be $\pm$0.06 mg/L (percent relative standard deviation* of 5.9%).

3. **Total Suspended Solids (SM #2540 D)**

The measurement of suspended solids, or suspended matter, in wastewater at various stages in the treatment gives a good indication of the efficiency of treatment. Total suspended solids may be determined by filtering a sample through a glass fiber filter and drying the residue to constant weight at 103- 105°C.

This lab uses a Gooch filter apparatus attached to a water aspirator. Other apparatus used in the determination include a drying oven, an analytical balance, and a desiccator. The funnel and glass fiber disk are first dried at 103-5°C for an hour, cooled in a desiccator to room temperature, and weighed. The sample (100, 50, or 25 milliliters, depending on expected suspended matter content, which should yield between 2.5 and 200 milligrams of TSS) is filtered through the glass fiber disk, and the funnel and disk are again dried, desiccated, and weighed. The cycle of drying, cooling, desiccating, and weighing is repeated until a constant weight is obtained or until the weight loss is less than 4% of the previous weight or 0.5 mg, whichever is less. Difference in the two weights is the amount of suspended solids in the sample.

From a standpoint of quality control, the analytical balance is the most important instrument although care must be taken to assure the drying oven is actually operating at 103-5°C, and that the desiccator is free from moisture (i.e., silica gel is replaced as required). This is a relatively imprecise procedure with the percent relative standard deviation reaching 33% for some concentrations.

4. **Biological Oxygen Demand (SM #5210 B)**

This test measures the amount of organic material in a sample by measuring the oxygen consumed by microorganisms in biodegrading organic constituents in the sample. BOD is an important measure of the quality of discharged water as high BOD can result in undesirable effects (oxygen depletion) on receiving waters. The test is part biological, and part chemical. The biological part cannot be calibrated, but the chemical part which consists of measuring dissolved oxygen (DO) before and after an incubation period, can. DO is normally measured with a DO meter which is periodically checked using an iodometric titration (i.e., Winkler) procedure.

Samples analyzed in this lab generally are in the 6.5 to 7.5 pH range, normally have not been chlorinated or oxidized by ozone, have not been biologically treated, are not extremely hot or cold, do not contain toxics, and do not contain supersaturated dissolved oxygen. Therefore, FWWTP samples normally do not required any special pretreatment as described in standard methods. When residual chlorine is present, as it sometimes is, the dechlorination procedure in Standard Method 507-52(2) is done prior to BOD analysis. Past experience has shown that samples often contain materials which are not degraded at normal rates by the microorganisms in settled sewage at the FWWTP. It is therefore necessary to seed BOD samples taken in the

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* Percent relative standard deviation (%RSD) is the same as coefficient of variation except that the latter is expressed as a decimal rather than a percent. %RSD = 100 x standard deviation ÷ mean.

final settling tank effluent (as in paragraph 5d, Method 507, Standard Methods, Ed. 16). To standardize BOD procedures in the lab, all BOD samples are seeded. Source of the seed is settled effluent from the primary treatment process.

If oxygen demand is expected to be greater than 8 mg/L (and it generally is in the wastewater treatment plant served by this lab), the sample must be diluted. Amount of sample added to a 300-mL bottle is determined from Table D-1 below. Care must be taken in adding dilution water to avoid air bubbles which would contribute to the DO determination. Dilution water is aerated by agitation and stored overnight in the incubator to make sure it is at approximately 20°C when used. Buffers are added the morning of the test by gentle agitation with care not to introduce air bubbles into the dilution water.

Each test includes a DO determination on a bottle containing only dilution water (i.e., a blank to make sure reagent grade water used in the lab does not contain BOD). DO is measured at the beginning of the test and after a 5-day incubation period. Incubation is in the dark at 20 ± 1°C (as measured with a certified thermometer). During periods when BOD may vary widely, an additional set of diluted bottles is prepared. The second set contains double the amount of sample as determined from the dilution chart (Table D-1). This is to assure there is some DO to measure at the end of the incubation period.

In typical intra-laboratory tests of natural water samples plus an exact increment of biodegradable organic compounds, mean values of 2.1 and 175 mg/L BOD with respective standard deviations were ± 0.7 and ± 26 mg/L (relative standard deviation of 33% and 15%) were obtained.

TABLE D-1 - BOD Dilutions

Sample Added to 300 mL BOD Bottle	Expected BOD Range Minimum (mg/L)	Maximum (mg/L)
3	210	560
6	105	280
9	70	187
12	53	140
15	42	112
18	35	94
21	30	80
24	26	70
27	24	62
30	21	56
45	14	37
60	11	28
75	8	22
150	4	12

5. **Fecal Coliforms (SM #9222 D)**

Fecal coliforms are found only in the gut and feces of warm- blooded animals. Determination of fecal coliforms in wastewater is a principal indicator of sanitary quality of the water and the effectiveness of the treatment process. The FWWTP lab takes special care in following standard methods pertaining to condition of laboratory apparatus, washing and sterilization, preparation of media, materials, distilled water, media specifications, and sampling.

Samples for fecal coliform tests must be taken in sterile bottles. The bottles should be wide-mouthed, made of glass or plastic, of any suitable size and shape. Ground-glass or rubber stoppered bottles are preferred but, if they are not available, polypropylene bottles of sufficient thickness that they can be sterilized repeatedly may be used. Bottles and all other glassware are cleansed thoroughly with detergent/hot water, rinsed with hot water, rinsed with distilled water, and sterilized for 60 minutes or more at 170°C. Sterilization indicator tape (e.g., Scientific Products Autoclave Indicator Tape) is used on all autoclaved labware. Sodium thiosulfate is added to each bottle if the bottles are to be used for sampling chlorinated wastewaters. Samples should be analyzed immediately after collection, but, if necessary, may be stored at 4°C and analyzed within six hours of the time the sample was taken.

This lab uses Whatman Type HC filters which are specially designed to enhance recovery of coliforms stressed by chlorine. It uses disposable, plastic culture dishes, commercially-prepared M-FC broth with rosolic acid inhibitor as a culture media, and incubation conditions of 24 $\pm$ 2 hours at 44.5 $\pm$ 0.2°C. A heat sink dry incubator is used preferentially; a water bath providing a uniform 44.5°C is available if needed. If comparison tests with labs using MPN techniques do not show good comparability, the lab goes to the two-step temperature incubation described in the method, and makes its own broth omitting rosolic acid, both these steps intended to enhance recovery of stressed coliforms.

When incubation is complete, fecal coliform cultures are removed from the incubator and counted within 20 minutes, with the aid of a dissecting micro-scope as necessary. All partially or totally blue colonies are counted. Grey-to-cream colonies indicate nonfecal coliforms and are not counted.

NOTES

These notes are not intended to be part of the lab's QA manual. They are intended to give guidance on options for what goes in the manual in places where the lab might want to do their own manual differently.

/1 This model manual contains QC information for plant operations (i.e., process control) as well as lab operations. The Lab Accreditation Program is interested primarily in lab QC, and the QA manual could cover only lab QC. But it is probably more convenient for the plant, given the close relationship between lab operations and process control, to also include process control QC in this manual.

/2 The lab should insert its own time schedule.

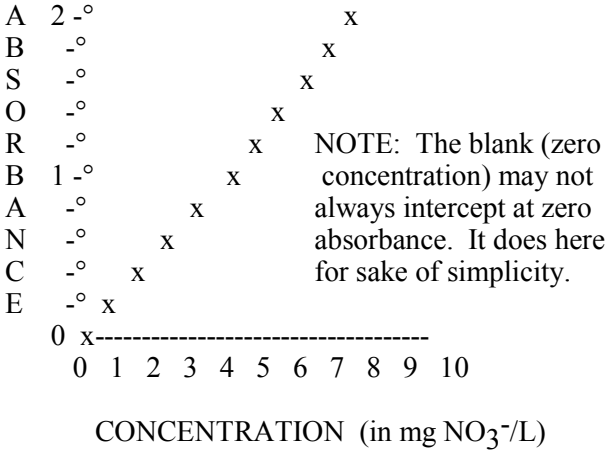
/3 Methods cited in this manual are for example only. If other approved methods are used, the manual should specify what they are. If "Standard Methods" is used, 40 CFR 136 requires Edition 17 or later.

/4 If only Winkler titrations are done in the lab, omit the statement about calibration of the DO meter.

/5 Some labs may have a need for calibration curves, e.g., for spectrophotometric determinations of nitrate or other nutrients. Those which do should add something like the following to their QA manual:

"The only parameter requiring a calibration curve (a plot showing relationship between instrument response and concentration) is nitrate. A visible spectrophotometric method is used (EPA Method 352.1) which requires the preparation of a calibration curve, sometimes called "standardization" or "standard calibration". For the nitrate curve, which is a fixed calibration curve (i.e., a curve used batch after batch until there is a reason to construct a new curve, a series of standards at concentrations of 0 (blank), 0.5, 1.5, 2.5, 3.5, 5.0, 7.5, and 10.0 in mg NO_3^-/L are analyzed and the absorbances obtained are plotted versus concentration. A hypothetical calibration curve is shown below. Concentrations for subsequent sample analyses are read directly from the calibration curve. The curve is used until an analysis of a check standard indicates it is no longer valid. A new curve is also prepared with every new batch of reagents or new standard solution.

HYPOTHETICAL CALIBRATION CURVE



/6 Distilled water may be purchased if it is of sufficient quality to meet lab needs.

/7 The purpose of using phosphate-free detergent is to protect the environment and has nothing to do with QA/QC in the lab.

/8 If Winkler titrations are used rather than a DO meter, the titration requires standardization of a sodium thiosulfate solution with potassium biniodate as described in the method.

/9 Before purchasing a certified thermometer, consider that, when they visit the lab for the on-site audit, Ecology can calibrate any good thermometer with 1°C or less increments. The same applies to the thermometer used in the fecal coliform incubator except that the increments must be 0.2°C or less).

/10 Prepared standards can be purchased from Hach, North Central Laboratories, and others. Call Ecology's QA Section if you have questions on how to purchase or use the standards.

/11 The standard suspension for the TSS test can be made from finely pulverized cellulose (available from, for example, Sigma Chemical Company, (800) 325-3010, as Type 20 cellulose, or from Aldrich, (800) 558-9160, as cellulose powder, 20 micron). The control suspension is made in a concentration of approximately 30 mg/L which is typical of the waste samples analyzed in some WTP labs. Five liters are made at a time by slowly adding 150 milligrams to 100 mL of warm water (35-55°C) while stirring on a hot plate/magnetic stirrer. After the cellulose is thoroughly wetted and the mixture is homogeneous, it is allowed to cool to room temperature and diluted to a final volume of 5.0 liters. The suspension is kept in a polyethylene (or Naglene) container and agitated immediately before use just as actual samples are. The container should be emptied and cleaned when about two- thirds empty.

/12 The frequency of the TSS standard test (as well as pH and residual chlorine) is up to the lab to determine, although it should be often enough so the lab can monitor its performance and know when it is out of control. The BOD standard test (glucose/glutamic acid or a substitute such as KHP) should be run every batch in accordance with the method. Frequency of duplicates is also up to the lab.

/13 Control charts are strongly recommended Ecology because they are a very practical mechanism for assuring that an analytical procedure is in control. The charts used as examples in this model QA manual are based on standard deviations. There are other, perhaps simpler, charts such as those based on range which are explained in "Standard Methods" and other references. Control charts should be used by any lab which is interested in the quality of its work.

/14 The lab should document the exact procedures used for each test performed in the lab to make sure they are done the same way time after time. These documents may be in the form of SOPs (standard operating procedures), or can be part of the QA manual such as the summary used in this model.

/15 If the lab uses the DPD method (SM 4500-Cl G), the last sentence in this paragraph could be replaced with "The liberated iodine is measured with a colorimeter according to instructions published by the instrument manufacturer." The second paragraph (at the top of page 18) should be deleted. The last paragraph should be replaced by "In a study involving 25 laboratories analyzing a 0.66 mg/L sample, the percent relative standard deviation * was 27.6% and the relative error was 15.6%.